

1 **LUBRICATING OIL HAVING ENHANCED**
2 **RESISTANCE TO OXIDATION, NITRATION**
3 **AND VISCOSITY INCREASE**

5 **BACKGROUND**

6 This invention relates to an antioxidant system and lubricating oil
7 comprising the antioxidant system. The lubricating oil of this invention may be
8 used as a lubricant for any lubricating application, however its enhanced
9 properties makes it particularly applicable for use as a lubricant for natural gas
10 fueled engines.

11 Natural gas fueled engines are engines that use natural gas as a fuel
12 source. Lubricating oil with high resistance to oxidation, nitration and viscosity
13 increase is preferred for lubricating oils used in natural gas engines because
14 of the conditions related to this type of engine.

15 Natural gas has a higher specific heat content than liquid hydrocarbon
16 fuels and therefore it burns hotter than liquid hydrocarbon fuels under typical
17 conditions. In addition, since it is already a gas, natural gas does not cool the
18 intake air by evaporation as liquid hydrocarbon fuel droplets do. Furthermore,
19 many natural gas fueled engines are run either at or near stoichiometric
20 conditions, where less excess air is available to dilute and cool combustion
21 gases. As a result, natural gas fueled engines generate higher combustion
22 gas temperatures than engines burning liquid hydrocarbon fuels. Since the
23 rate of formation of NO_x increases exponentially with temperature, natural gas
24 fueled engines may generate NO_x concentrations high enough to cause
25 severe nitration of lubricating oil.

26 In most cases, natural gas fueled engines are used continuously at
27 70 to 100% load, whereas an engine operating in vehicular service may only
28 spend 50% of its time at full load. Lubricating oil drain intervals may vary in
29 vehicular service, but are typically shorter than those for natural gas fueled
30 engines.

31 Natural gas fueled engines may be located in remote areas where
32 service is not readily available and may be expensive. Because of this it is
33 important to ensure the reliability of natural gas fueled engines. High

1 resistance to oxidation and nitration is therefore required for lubricating oils
2 used in natural gas engines.

3 Good valve wear control is important for keeping engine operating
4 costs down and may be achieved by providing the proper amount and
5 composition of ash. Minimizing combustion chamber deposits and spark plug
6 fouling are also considerations in setting the ash content and composition in
7 these oils. Lubricating oil ash levels are limited, so detergents must be
8 carefully selected to minimize piston deposits and ring sticking. Good wear
9 protection is required to prevent scuffing and corrosion.

10 If lubricating oils for natural gas fueled engines are not formulated to
11 handle typical environments for those engines, the lubricating oil will
12 deteriorate rapidly during use. This deterioration will typically cause the
13 lubricating oil to thicken which results in engine sludge, piston deposits, oil
14 filter plugging, and in severe cases, accelerated ring and liner wear.

15 The general industry approach to reduce deterioration of lubricating oil
16 and the resultant engine sludge, piston deposits, oil filter plugging and
17 accelerated ring and liner wear is to add antioxidants such as hindered phenols
18 as well as diphenyl amines and sulfurized compounds. Increasing the amount
19 of these antioxidants in lubricating oil is increasingly effective to avoid
20 lubricating oil deterioration. But at some point the solubility limit of the additive
21 reaches maximum effectiveness and detrimental effects can be also noticed in
22 piston deposit control.

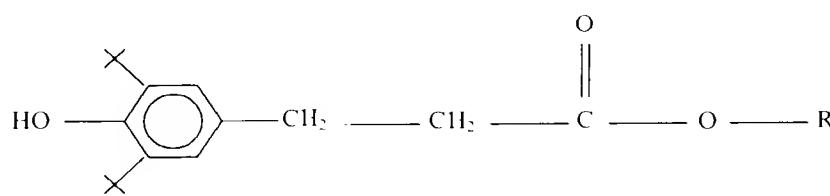
23 While it is no surprise that increasing the amount of antioxidant is
24 effective in increasing the antioxidant properties of a finished oil, the
25 antioxidant system of this invention provides a method to enhance the
26 antioxidant properties without increasing the amount of antioxidant. This
27 method involves use of an antioxidant system that comprises sulfurized
28 isobutylene and an antioxidant system that comprises sulfurized isobutylene
29 and hindered phenol.

30

31 SUMMARY

32 One embodiment of this invention comprises an antioxidant system
33 comprising sulfurized isobutylene. Another embodiment of this invention

1 comprises an antioxidant system comprising sulfurized isobutylene and one or
2 more hindered phenols. The hindered phenols of this antioxidant system may
3 comprise butylated hydroxy toluene (BHT), 3,5-di-t-butyl 4-hydroxy phenol
4 propionate and one or more antioxidants have the general formula:



11 Another embodiment of this invention is an additive formulation comprising
12 one or more of the additive systems of this invention and other additives.

13 The lubricating oil of this invention may comprise base oil and one or
14 more of the additive formulations of this invention. The lubricating oil of this
15 invention may comprise base oil and one or more of the additive systems of
16 this invention. One embodiment of this invention may comprise a method of
17 lubricating engines comprising contacting one or more of the lubricating oils of
18 this invention with one or more engines. One embodiment of this invention
19 may comprise a method of lubricating natural gas fueled engines comprising
20 contacting one or more of the lubricating oils of this invention with one or more
21 natural gas fueled engines. This invention comprises methods for making any
22 embodiments of the lubricating oil or additive systems or additive formulations
23 of this invention comprising combining the components in any order at a
24 temperature sufficient to encourage mixing of the components, but not
25 sufficient to degrade the components. This invention comprises methods for
26 making any embodiments of the lubricating oil of this invention comprising
27 combining the components in any order at a temperature of about
28 140 degrees F.

DETAILED DESCRIPTION OF THE INVENTION

This invention is directed to one or more antioxidant systems for use in lubricating oils. One embodiment of the invention may be lubricating oil that comprises sulfurized isobutylene as an antioxidant. Another embodiment of

1 the invention may be an additive formulation that comprises sulfurized
2 isobutylene as an antioxidant, and one or more dispersants, one or more
3 detergents, and one or more wear inhibitors. Another embodiment of this
4 invention may be lubricating oil comprising one or more of the antioxidant
5 systems of this invention. Another embodiment of this invention may be a
6 lubricating oil comprising one or more of the additive formulations of this
7 invention. These antioxidant systems, additive formulations and lubricating
8 oils may be particularly useful in natural gas fueled engines.

9 Another embodiment of the invention may be lubricating oil that
10 comprises sulfurized isobutylene in combination with an antioxidant such as
11 hindered phenol. One embodiment of the invention may be an additive
12 formulation that comprises sulfurized isobutylene, an antioxidant such as
13 hindered phenol, and one or more dispersants, one or more detergents, and
14 one or more wear inhibitors. Another embodiment of this invention may be
15 lubricating oil comprising one or more of the antioxidant systems of this
16 invention. Another embodiment of this invention may be lubricating oil
17 comprising one or more of the additive formulations of this invention. These
18 antioxidant systems, additive formulations and lubricating oils may be
19 particularly useful in natural gas fueled engines.

20 Another embodiment of this invention may be a method to make a
21 lubricating oil comprising the antioxidant systems of this invention by
22 combining the components and mixing them together and heating at a
23 temperature sufficient to encourage mixing of the components, but not
24 sufficient to degrade the components. Another embodiment of this invention is
25 a method of using the lubricating oils of this invention to lubricate an engine
26 by contacting the engine with the lubricating oil of this invention. Another
27 embodiment of this invention is a method of using the lubricating oils of this
28 invention to lubricate a natural gas engine by contacting a natural gas engine
29 with the lubricating oil of this invention.

30

31 **I. ANTIOXIDANT SYSTEM**

32 One embodiment of the antioxidant system of this invention may
33 comprise sulfurized isobutylene. Lubricating oils of this invention may

1 comprise this additive system. Lubricating oil comprising this antioxidant
2 system may comprise about 0.02 wt. % to about 2 wt. % sulfurized
3 isobutylene.

4 Another embodiment of the antioxidant system of this invention may
5 comprise the hindered phenols described herein and sulfurized isobutylene.
6 Lubricating oils of this invention may comprise this additive system. The
7 preferred concentration ratio of the sulfurized isobutylene to the hindered
8 phenol of this antioxidant system may be about 0.002 to about 2.5, more
9 preferred about 0.004 to about 1.13. A lubricating oil comprising this
10 antioxidant system may comprise about 0.21 wt. % to about 6.50 wt. %, more
11 preferably about 0.42 wt. % to about 5.45 wt. % of an antioxidant system
12 comprising sulfurized isobutylene and one or more hindered phenols
13 described herein.

14 When wt. % is used herein it refers to wt. % of lubricating oil unless
15 otherwise defined.

16

17 **A. Sulfurized Isobutylene**

18 Sulfurized isobutylene is known by those skilled in the art to be an
19 extreme pressure agent, effective in preventing wear in high pressure
20 environments such as gear lubrication. This invention is based on the finding
21 that when sulfurized isobutylene is used alone or in combination with
22 traditional antioxidants such as hindered phenols, there is an improvement in
23 oxidation, nitration and percent viscosity increase measurements. Using
24 sulfurized isobutylene in a lubricant for engines and for natural gas fueled
25 engines in particular is different than using sulfurized isobutylene as an
26 extreme pressure agent in lubricating oil for gear applications. Sulfurized
27 isobutylene used as an anti wear agent in gear applications is not typically
28 exposed to combustion gases and water, whereas sulfurized isobutylene used
29 as an antioxidant in lubricants for natural gas fueled engines or any engine
30 may typically be exposed to combustion gases and water in the form of
31 condensation.

32 Sulfurized isobutylene comprises a long chain hydrocarbon that is
33 reacted with a various sulfur compounds that are incorporated into the chain.

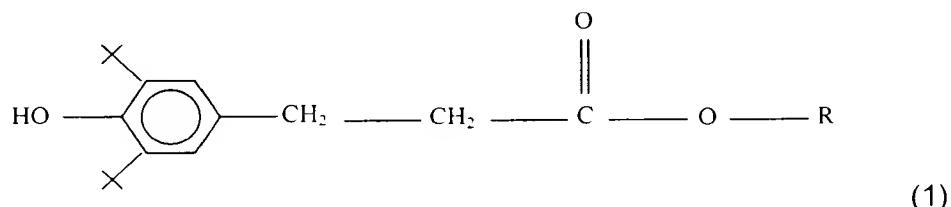
1 This provides an oil soluble compound that is effective in providing extreme
2 pressure (EP) protection.

3 Sulfurized isobutylene for use in certain embodiments of this invention
4 may include one or more of sulfurized isobutylenes such as
5 Mobilad C-100 and R.T. Vanderbilt Vanlube SB. One embodiment of the
6 invention may be a lubricating oil that comprises less than about
7 2 wt. % sulfurized isobutylene.

8 One embodiment of the lubricating oil of this invention may comprise
9 an antioxidant system comprising about 0.02 wt. % to about 2 wt. % sulfurized
10 isobutylene or preferably about 0.04 wt. % to about 1.75 wt. % sulfurized
11 isobutylene. Another embodiment of the lubricating oil of this invention may
12 comprise an antioxidant system comprising the hindered phenols described
13 herein and about 0.01 weight percent (wt. %) to about 0.5 wt. %, more
14 preferably from about 0.02 wt. % to about 0.45 wt. % sulfurized isobutylene.
15

16 **B. Hindered Phenol**

17 Embodiments of this invention may comprise hindered phenols. Liquid
18 hindered phenols are preferred. Preferred hindered phenols include one or
19 more hindered phenols having the general formula:



The lubricating oil of this invention may comprise about 0.10 wt. % to about 3.0 wt. %, preferably from about 0.20 wt. % to about 2.50 wt. % of one or more hindered phenols of the general formula (1).

A preferred antioxidant system of this invention comprises 3,5-di-t-butyl 4-hydroxy phenol propionate. The lubricating oil of this invention may comprise about 0.10 wt. % to about 3.0 wt. %, preferably from about 0.20 wt. % to about 2.50 wt. % 3,5-di-t-butyl 4-hydroxy phenol propionate.

1 A most preferred antioxidant of this invention is commercially available
2 from Ciba Specialty Chemicals at 540 White Plains Road, Terrytown,
3 New York 10591 as IRGANOX L 135® or Crompton Corporation at
4 199 Benson Road, Middlebury, CT 06749 as Naugard®PS-48.
5 IRGANOX L 135® and Naugard®PS-48 are liquid high molecular weight
6 phenolic antioxidants. The lubricating oil of this invention may comprise about
7 0.10 wt. % to about 3.0 wt. %, preferably from about 0.20 wt. % to about
8 2.50 wt. % include IRGANOX L 135®.

9 Embodiments of this invention may comprise butylated hydroxy
10 toluene (BHT). The lubricating oil of this invention may comprise about
11 0.10 wt. % to about 3.0 wt. % BHT and preferably about 0.20 wt. % to about
12 2.50 wt. % BHT.

13 The lubricating oil of this invention may comprise combined BHT and
14 other hindered phenols described herein. This combination may be present in
15 about 0.20 wt. % to about 6.00 wt. %, more preferably about 0.40 wt. % to
16 about 5.00 wt. % of the finished oil.

17

18 II. ADDITIVE FORMULATION

19 When incorporated in lubricating oil, certain embodiments of the
20 additive formulation of this invention may provide enhanced oxidation
21 inhibition, nitration inhibition, total base retention, reduction in acid formation
22 and reduction in percent viscosity increase. The additive formulation of this
23 invention may comprise one or more of the antioxidant systems described
24 herein.

25 Another embodiment of the additive formulation of this invention may
26 comprise butylated hydroxy toluene, sulfurized isobutylene, one or more
27 detergents, one or more dispersants, one or more wear inhibitors and one or
28 more of 3,5-di-t-butyl 4-hydroxy phenol propionate and hindered phenols
29 having the general formula (1). Other traditional additives may be used.

30 Another embodiment of the additive formulation of this invention may
31 comprise sulfurized isobutylene, one or more detergents, one or more
32 dispersants and one or more wear inhibitors. Other traditional additives may
33 be used.

1 Another embodiment of the additive formulation of this invention may
2 comprise sulfurized isobutylene, one or more detergents, one or more
3 dispersants, one or more wear inhibitors and one or more of 3,5-di-t-butyl
4 4-hydroxy phenol propionate and hindered phenols having the general
5 formula (1). Other traditional additives may be used.

6 The additive formulation of this invention may comprise diluent oil. It is
7 known in the art to add diluent oil to additive formulations and this is called
8 "trimming" the additive formulation. A preferred embodiment may be trimmed
9 with any diluent oil typically used in the industry. This diluent oil may be a
10 Group I, II, III, IV or V oil. A preferred amount of diluent oil may comprise
11 about 4.00 wt. %.

12

13 **III. OTHER ADDITIVE COMPONENTS**

14 The following additive components are examples of some of the
15 components that may be favorably employed in the present invention in
16 addition to the antioxidant system of this invention. These examples of
17 additives are provided to illustrate the present invention, but they are not
18 intended to limit it.

19

20 **A. Detergent**

21 Any detergents commonly used in lubricating oils may be used in this
22 invention. These detergents may or may not be overbased detergents or they
23 may be low, neutral, medium, or high overbased detergents. For example,
24 detergents of this invention may comprise sulfonates, salicylates and
25 phenates. Metal sulfonates, salicylates and phenates are preferred. When the
26 term metal is used with respect to sulfonates, salicylates and phenates herein,
27 it refers to calcium, magnesium, lithium, magnesium, potassium and barium.

28 The lubricating oil of this invention may comprise about 1.0 wt. % to
29 about 8.5 wt. %, preferably about 2 wt. % to about 6 wt. % of one or more
30 detergents.

1

2 **B. Additional Antioxidants**

3 If desired, additional antioxidants may be used. Other antioxidants may
4 reduce the tendency of mineral oils to deteriorate in service. In addition to the
5 antioxidant systems of this invention, the additive formulation may also
6 include but is not limited to such antioxidants as phenol type (phenolic)
7 oxidation inhibitors, such as 4,4'-methylene-bis(2,6-di-tert-butylphenol),
8 4,4'-bis(2,6-di-tert-butylphenol), 4,4'-bis(2-methyl-6-tert-butylphenol),
9 2,2'-methylene-bis(4-methyl-6-tert-butylphenol),
10 4,4'-butyldene-bis(3-methyl-6-tert-butylphenol),
11 4,4'-isopropylidene-bis(2,6-di-tert-butylphenol),
12 2,2'-methylene-bis(4-methyl-6-nonylphenol),
13 2,2'-isobutylidene-bis(4,6-dimethylphenol),
14 2,2'-methylene-bis(4-methyl-6-cyclohexylphenol),
15 2,6-di-tert-butyl-4-methylphenol, 2,6-di-tert-butyl-4-ethylphenol,
16 2,4-dimethyl-6-tert-butyl-phenol, 2,6-di-tert-l-dimethylamino-p-cresol,
17 2,6-di-tert-4-(N,N'-dimethylaminomethylphenol),
18 4,4'-thiobis(2-methyl-6-tert-butylphenol),
19 2,2'-thiobis(4-methyl-6-tert-butylphenol),
20 bis(3-methyl-4-hydroxy-5-tert-butylbenzyl)-sulfide, and
21 bis(3,5-di-tert-butyl-4-hydroxybenzyl). Diphenylamine-type oxidation inhibitors
22 include, but are not limited to, alkylated diphenylamine,
23 phenyl-.alpha.-naphthylamine, and alkylated-.alpha.-naphthylamine. Other
24 types of oxidation inhibitors include metal dithiocarbamate (e.g., zinc
25 dithiocarbamate), and methylenebis (dibutyl dithiocarbamate).

26

27 **C. Wear Inhibitors**

28 Traditional wear inhibitors may be used in this invention. As their name
29 implies, these agents reduce wear of moving metallic parts. Examples of such
30 agents include, but are not limited to phosphates, phosphites, carbamates,
31 esters, sulfur containing compounds, and molybdenum complexes. The
32 finished lubricating oil of this invention may comprise one or more wear
33 inhibitors such metal dithiophosphates and metal dithiocarbamates or mixtures

1 thereof. A preferred wear inhibitor for use in this invention comprises zinc
2 dithiophosphate. Lubricating oil of this invention may comprise about
3 0.2 wt. % to about 1.5 wt. % or preferably about 0.3 wt. % to about
4 0.8 wt. % of one or more wear inhibitors.

5

6 **D. Rust Inhibitors (Anti-Rust Agents)**

7 Nonionic polyoxyethylene surface active agents: polyoxyethylene lauryl
8 ether, polyoxyethylene higher alcohol ether, polyoxyethylene nonyl phenyl
9 ether, polyoxyethylene octyl phenyl ether, polyoxyethylene octyl stearyl ether,
10 polyoxyethylene oleyl ether, polyoxyethylene sorbitol monostearate,
11 polyoxyethylene sorbitol mono-oleate, and polyethylene glycol mono-oleate
12 may be used.

13 Other compounds such as stearic acid and other fatty acids,
14 dicarboxylic acids, metal soaps, fatty acid amine salts, metal salts of heavy
15 sulfonic acid, partial carboxylic acid ester of polyhydric alcohol, and
16 phosphoric ester may be used.

17

18 **E. Demulsifiers**

19 Addition product of alkylphenol and ethylene oxide, polyoxyethylene
20 alkyl ether, and polyoxyethylene sorbitan ester may be used.

21

22 **F. Extreme Pressure Agents (EP Agents)**

23 Zinc dialkyldithiophosphate (primary alkyl, secondary alkyl, and aryl
24 type), sulfurized oils, diphenyl sulfide, methyl trichlorostearate, chlorinated
25 naphthalene, fluoroalkylpolysiloxane, and lead naphthenate may be used.

26

27 **G. Friction Modifiers**

28 Fatty alcohol, fatty acid, amine, borated ester, and other esters may be
29 used.

30

31 **H. Multifunctional Additives**

32 Sulfurized oxymolybdenum dithiocarbamate, sulfurized
33 oxymolybdenum organo phosphorodithioate, oxymolybdenum monoglyceride,

1 oxymolybdenum diethylate amide, amine-molybdenum complex compound,
2 and sulfur-containing molybdenum complex compound may be used.

3

4 **I. Viscosity Index Improvers**

5 Polymethacrylate type polymers, ethylene-propylene copolymers,
6 styrene-isoprene copolymers, hydrated styrene-isoprene copolymers,
7 polyisobutylene, and dispersant type viscosity index improvers may be used.

8

9 **J. Pour Point Depressants**

10 Polymethyl methacrylate may be used.

11

12 **K. Foam Inhibitors**

13 Alkyl methacrylate polymers and dimethyl silicone polymers may be
14 used.

15

16 **L. Dispersants**

17 A preferred embodiment of the lubricating oil of this invention may
18 comprise one or more nitrogen containing dispersants of the type generally
19 represented by succinimides (e.g., polyisobutylene succinic acid/anhydride
20 (PIBSA)-polyamine having a PIBSA molecular weight of about 700 to
21 2500). The dispersants may be borated or non-borated, ashless or ash
22 containing. Lubricating oils of this invention may comprise about 1 wt. % to
23 about 8 wt. % or more preferably about 1.5 wt. % to about 6 wt. of one or more
24 dispersants.

25 Preferred dispersants for this invention comprise one or more
26 dispersants having an average molecular weight (mw) of about 1000 to about
27 5000. Dispersants prepared from polyisobutylene (PIB) having a mw of about
28 1000 to about 5000 are such preferred dispersants.

29 A preferred dispersant of this invention may be a one or more
30 succinimides. The term "succinimide" is understood in the art to include many
31 of the amide, imide, etc. species that are also formed by the reaction of a
32 succinic anhydride with an amine and is so used herein. The predominant
33 product, however, is succinimide and this term has been generally accepted

1 as meaning the product of a reaction of an alkenyl- or alkyl-substituted
2 succinic acid or anhydride with a polyamine. Alkenyl or alkyl succinimides are
3 disclosed in numerous references and are well known in the art. Certain
4 fundamental types of succinimides and related materials encompassed by the
5 term of art "succinimide" are taught in U.S. Pat. Nos. 2,992,708; 3,018,250;
6 3,018,291; 3,024,237; 3,100,673; 3,172,892; 3,219,666; 3,272,746;
7 3,361,673; 3,381,022; 3,912,764; 4,234,435; 4,612,132; 4,747,965;
8 5,112,507; 5,241,003; 5,266,186; 5,286,799; 5,319,030; 5,334,321;
9 5,356,552; 5,716,912, the disclosures of which are hereby incorporated by
10 reference.

11 This invention may comprise one or more succinimides, which may be
12 either a mono or bis-succinimide. This invention may comprise lubricating oil
13 involving one or more succinimide dispersants that have or have not been
14 post treated.

15

16 **IV. GROUP I, II, III, IV AND V BASE OIL**

17 Base Oil as used herein is defined as a base stock or blend of base
18 stocks. Base Stock as used herein is defined as a lubricant component that is
19 produced by a single manufacturer to the same specifications (independent of
20 feed source or manufacturers location that meets the same manufacturer's
21 specification and that is identified by a unique formula, product identification
22 number, or both. Base stocks may be manufactured using a variety of
23 different processes including but not limited to distillation, solvent refining,
24 hydrogen processing, oligomerization, esterification, and rerefining. Rerefined
25 stock shall be substantially free from materials introduced through
26 manufacturing, contamination, or previous use. The base oil of this invention
27 may be any natural or synthetic lubricating base oil fraction particularly those
28 having a kinematic viscosity at 100 degrees Centigrade (C) and about
29 5 centistokes (cSt) to about 20 cSt, preferably about 7 cSt to about
30 16 cSt, more preferably about 9 cSt to about 15 cSt. Hydrocarbon synthetic
31 oils may include, for example, oils prepared from the polymerization of
32 ethylene, i.e., polyalphaolefin or PAO, or from hydrocarbon synthesis
33 procedures using carbon monoxide and hydrogen gases such as in a

1 Fisher-Tropsch process. A preferred base oil is one that comprises little, if
2 any, heavy fraction; e.g., little, if any, lube oil fraction of viscosity 20 cSt or
3 higher at 100 degrees C.

4 The base oil may be derived from natural lubricating oils, synthetic
5 lubricating oils or mixtures thereof. Suitable base oil includes base stocks
6 obtained by isomerization of synthetic wax and slack wax, as well as
7 hydrocrackate base stocks produced by hydrocracking (rather than solvent
8 extracting) the aromatic and polar components of the crude. Suitable base oils
9 include those in API categories I II, III, and IV. Saturates levels and viscosity
10 indices for Group I, II and III base oils are listed in Table 1. Group IV base oils
11 are polyalphaolefins (PAO). Group V base oils include all other base oils not
12 included in Group I, II, III, or IV. Suitable base oils may include those in
13 API categories I, II, III, and IV as defined in API Publication 1509,
14 14th Edition Addendum I, December 1998.

15
16 **TABLE 1**

17 **Saturates, Sulfur and Viscosity Index of**
18 **Group I, II and III Base Stocks**

Group	Saturates (As determined by ASTM D 2007) Sulfur (As determined by ASTM D 2270)	Viscosity Index (As determined by ASTM D 4294, ASTM D 4297 or ASTM D 3120)
I	Less than 90 % saturates and/or Greater than to 0.03 % sulfur	Greater than or equal to 80 and less than 120
II	Greater than or equal to 90 % saturates and less than or equal to 0.03 % sulfur	Greater than or equal to 80 and less than 120
III	Greater than or equal to 90 % saturates and less than or equal to 0.03% sulfur	Greater than or equal to 120

19
20 Natural lubricating oils may include animal oils, vegetable oils
21 (e.g., rapeseed oils, castor oils and lard oil), petroleum oils, mineral oils, and
22 oils derived from coal or shale.

23 Synthetic oils may include hydrocarbon oils and halo-substituted
24 hydrocarbon oils such as polymerized and inter-polymerized olefins,
25 alkylbenzenes, polyphenyls, alkylated diphenyl ethers, alkylated diphenyl
26 sulfides, as well as their derivatives, analogues and homologues thereof, and

1 the like. Synthetic lubricating oils also include alkylene oxide polymers,
2 interpolymers, copolymers and derivatives thereof wherein the terminal
3 hydroxyl groups have been modified by esterification, etherification, etc.
4 Another suitable class of synthetic lubricating oils comprises the esters of
5 dicarboxylic acids with a variety of alcohols. Esters useful as synthetic oils
6 also include those made from C₅ to C₁₂ monocarboxylic acids and polyols and
7 polyol ethers. Tri-alkyl phosphate ester oils such as those exemplified by
8 tri-n-butyl phosphate and tri-iso-butyl phosphate are also suitable for use as
9 base oils.

10 Silicon-based oils (such as the polyakyl-, polyaryl-, polyalkoxy-, or
11 polyaryloxy-siloxane oils and silicate oils) comprise another useful class of
12 synthetic lubricating oils. Other synthetic lubricating oils include liquid esters
13 of phosphorus-containing acids, polymeric tetrahydrofurans, polyalphaolefins,
14 and the like.

15 The base oil may be derived from unrefined, refined, rerefining oils, or
16 mixtures thereof. Unrefined oils are obtained directly from a natural source or
17 synthetic source (e.g., coal, shale, or tar sand bitumen) without further
18 purification or treatment. Examples of unrefined oils include a shale oil
19 obtained directly from a retorting operation, a petroleum oil obtained directly
20 from distillation, or an ester oil obtained directly from an esterification process,
21 each of which may then be used without further treatment. Refined oils are
22 similar to the unrefined oils except that refined oils have been treated in one
23 or more purification steps to improve one or more properties. Suitable
24 purification techniques include distillation, hydrocracking, hydrotreating,
25 dewaxing, solvent extraction, acid or base extraction, filtration, and
26 percolation, all of which are known to those skilled in the art. Rerefining oils
27 are obtained by treating used oils in processes similar to those used to obtain
28 the refined oils. These rerefining oils are also known as reclaimed or
29 reprocessed oils and often are additionally processed by techniques for
30 removal of spent additives and oil breakdown products.

31 Base oil derived from the hydroisomerization of wax may also be used,
32 either alone or in combination with the aforesaid natural and/or synthetic base

1 oil. Such wax isomerate oil is produced by the hydroisomerization of natural or
2 synthetic waxes or mixtures thereof over a hydroisomerization catalyst.

3 It is preferred to use a major amount of base oil in the lubricating oil of
4 this invention. A preferred range of base oil for this invention may be about
5 80 wt. % to about 97 wt. % of the lubricating oil. (When wt. % is used herein, it
6 is referring to wt. % of the lubricating oil unless otherwise specified.) A more
7 preferred embodiment of this invention may comprise an amount of base oil
8 that comprises about 85 wt. % to about 95 wt. % of the lubricating oil.
9

10 **V. FINISHED LUBRICATING OIL COMPRISING THE ADDITIVE
11 FORMULATION**

12 The following embodiments of finished lubricating oils are illustrative
13 only. The invention is not limited to these embodiments.

14 One embodiment of the lubricating oil of this invention may comprise
15 lubricating oil, the hindered phenols described herein and sulfurized
16 isobutylene. The components of the antioxidant systems of this invention and
17 other additives traditionally used in the industry may be incorporated in
18 lubricating oil in any manor either individually or in any combination.
19

20 One embodiment of the lubricating oil of this invention may comprise
21 about 0.21 wt. % to about 6.5 wt. %, more preferably about 0.42 wt. % to
22 about 5.45 wt. % of one or more of the antioxidant systems of this invention
23 comprising the hindered phenols described herein and sulfurized isobutylene.
24 Other additives traditionally used in the art may be included in the finished
25 lubricating oil of this invention.

26 One embodiment of the lubricating oil of this invention comprises a
27 major amount of one or more base oils, about 1 wt. % to about 8 wt. % of one
28 or more dispersants; about 1 wt. % to about 8.5 wt. % of one or more
29 detergents, about 0.2 wt. % to about 1.25 wt. % of one or more wear
30 inhibitors, about 0.01 wt. % to about 0.5 wt. % sulfurized isobutylene, and
31 about 0.2 wt. % to about 6 wt. % of one or more of the hindered phenols
32 described herein. This embodiment may be prepared by combining the
33 components with agitation until all components are mixed. The ingredients
34 may be combined in any order and at a temperature sufficient to blend the

1 components but not high enough to degrade the components. A temperature
2 of about 120 degrees F. to about 160 degrees F. may be used. It does not
3 matter whether the components are heated before after or during combining
4 them.

5 One embodiment of the lubricating oil of this invention comprises a
6 major amount of one or more base oils, about 1.25 wt. % to about 6 wt. % of
7 one or more dispersants; about 2 wt. % to about 6 wt. % of one or more
8 detergents, about 0.3 wt. % to about 0.8 wt. % of one or more wear inhibitors,
9 about 0.02 wt. % to about 0.45 wt. % sulfurized isobutylene, and about
10 0.4 wt. % to about 5 wt. % of one or more of the hindered phenols described
11 herein. This embodiment may be prepared by combining the components with
12 agitation until all components are mixed. The ingredients may be combined in
13 any order and at a temperature sufficient to blend the components but not
14 high enough to degrade the components. A temperature of about
15 120 degrees F. to about 160 degrees F. may be used. It does not matter
16 whether the components are heated before after or during combining them.

17 One embodiment of the lubricating oil of this invention comprises
18 lubricating oil comprising a major amount of one or more base oils, about
19 1 wt. % to about 8 wt. % of one or more dispersants, about 1 wt. % to about
20 8.5 wt. % of one or more detergents, about 0.2 wt. % to about 1.25 wt. % of
21 one or more wear inhibitors, and about 0.02 wt. % to about 2 wt. % sulfurized
22 isobutylene. This embodiment may be prepared by combining the
23 components with agitation until all components are mixed. The ingredients
24 may be combined in any order and at a temperature sufficient to blend the
25 components but not high enough to degrade the components. A temperature
26 of about 120 degrees F. to about 160 degrees F. may be used. It does not
27 matter whether the components are heated before after or during combining
28 them.

29 One embodiment of the lubricating oil of this invention comprises
30 lubricating oil comprising a major amount of one or more base oils, about
31 1.25 wt. % to about 6 wt. % of one or more dispersants, about 2 wt. % to
32 about 6 wt. % of one or more detergents, about 0.3 wt. % to about
33 0.8 wt. % of one or more wear inhibitors, and about 0.04 wt. % to about

1 1.75 wt. % sulfurized isobutylene. This embodiment may be prepared by
2 combining the components with agitation until all components are mixed. The
3 ingredients may be combined in any order and at a temperature sufficient to
4 blend the components but not high enough to degrade the components. A
5 temperature of about 120 degrees F. to about 160 degrees F. may be used. It
6 does not matter whether the components are heated before after or during
7 combining them.

8 One embodiment of the lubricating oil of this invention may have a
9 Total Base Number (TBN) of about 2.15 milligrams Potassium Hydroxide
10 per gram of sample (mg KOH/gr) to about 8.88 mg KOH/gr. A more preferable
11 embodiment would have a TBN from about 3.00 mg KOH/gr to about
12 8.00 mg KOH/gr. Unless otherwise specified, TBN, as used herein, is
13 determined by using the method ASTM D2896.

14 Another embodiment of this invention may comprise a method of
15 lubricating engines comprising contacting one or more engines with any
16 embodiment of the lubricating oil of this invention.

17 Another embodiment of this invention comprises a method of
18 lubricating natural gas engines comprising contacting one or more natural gas
19 engines with any embodiment of the lubricating oil of this invention.

20 Another embodiment of this invention comprises a method of
21 lubricating engines comprising lubricating one or more engines with any
22 embodiment of the lubricating oil of this invention.

23 Another embodiment of this invention comprises a method of
24 lubricating natural gas engines comprising lubricating one or more natural gas
25 engines with any embodiment of the lubricating oil of this invention.

26 Another embodiment of this invention comprises combining the
27 components of any embodiment of lubricating oil of this invention. This
28 embodiment may be accomplished by combining the components with
29 agitation until all components are mixed. The ingredients may be combined in
30 any order and at a temperature sufficient to blend the components but not
31 high enough to degrade the components. A temperature of about
32 120 degrees F. to about 160 degrees F. may be used. It does not matter
33 whether the components are heated before after or during combining them.

1

2 **VI. LUBRICATING OIL FOR NATURAL GAS FUELED ENGINES**

3 There is a difference in the lubricating oil requirements for natural gas
4 fueled engines and engines that are fueled by liquid hydrocarbon fuels. The
5 combustion of liquid hydrocarbon fuels such as diesel fuel often results in a
6 small amount of incomplete combustion (e.g., exhaust particulates). In a liquid
7 hydrocarbon fueled engine, these incombustibles provide a small but critical
8 degree of lubrication to the exhaust valve/seat interface, thereby ensuring the
9 durability of both cylinder heads and valves. The combustion of natural gas
10 fuel is often very complete, with virtually no incombustible materials.

11 Therefore, the durability of the cylinder head and valve is controlled by the
12 ash content and other properties of the lubricating oil and its consumption
13 rate. There are no incombustible materials to aid in lubrication to the exhaust
14 valve/seat interface in a natural gas fueled engine. Natural gas fueled engines
15 burn fuel that is introduced to the combustion chamber in the gaseous phase.
16 This has a significant affect on the intake and exhaust valves because there is
17 no fuel-derived lubricant for the valves like liquid droplets or soot.

18 Consequently, gas engines are solely dependent on the lubricant ash to
19 provide lubricant between the hot valve face and its mating seat. Too little ash
20 or the wrong type can accelerate valve and seat wear, while too much ash
21 may lead to valve guttering and subsequent valve torching. Too much ash can
22 also lead to detonation from combustion chamber deposits. Consequently,
23 gas engine builders frequently specify a narrow ash range that they have
24 learned provides the optimum performance. Since most gas is low in sulfur,
25 excess ash is generally not needed to address alkalinity requirements, and
26 ash levels are largely optimized around the needs of the valves. There may
27 be exceptions to this in cases where sour gas or landfill gas is used.

28 Natural gas fueled engine lubricating oils are classified according to
29 their ash content. Unless otherwise specified, ash contents discussed herein
30 were determined by ASTM D874. The lubricant ash acts as a solid lubricant to
31 protect the valve/seat interface in place of naturally occurring exhaust
32 particles in a hydrocarbon fueled engine. The oil industry has accepted
33 guidelines that classify natural gas fueled engine lubricating oil according to

1 their ash level. The classifications of natural gas fueled engine lubricating oil
2 according to their ash levels are presented in Table 2.

3

4 **TABLE 2**

5 **Classifications of Lubricating Oils for**
6 **Natural Gas Fueled Engines According To Ash Levels**

<u>Ash Designation</u>	<u>Sulfated Ash Level</u> (wt. % Determined by ASTM D874)
Ashless	0 < Ash < 0.15
Low Ash	0.15 < Ash < 0.6
Medium Ash	0.6 < Ash < 1.0
High Ash	Ash > 1.0

7

8 The ash level of lubricating oil is often determined by its formulation
9 components. Metal-containing detergents (e.g., barium, calcium) and
10 metallic-containing wear inhibitors contribute to the ash level of lubricating
11 oils. For correct engine operation, gas engine manufacturers define lubricating
12 oil ash requirements as part of the lubricating oil specifications. For example,
13 manufacturers of 2-cycle engines often require natural gas engine lubricating
14 oil to be Ashless to minimize the extent of harmful deposits that form on the
15 piston and combustion chamber area. Manufacturers of 4-cycle engines often
16 require natural gas engine lubricating oils to be Low, Medium or High Ash
17 levels, refer to Table 2, to provide the correct balance of engine cleanliness
18 and durability of the cylinder head and valves. Running the engine with
19 lubricating oil with too low an ash level will likely result in shortened life for the
20 valves or cylinder head. Running the engine with lubricating oil having too
21 high an ash level will likely cause excessive deposits in the combustion
22 chamber and upper piston area.

1 The degree of nitration of the lubricating oil may vary significantly
2 depending on the engine design and operating conditions. Lean burn engines
3 produce less NO_x than their stoichiometric counterparts, so they tend to
4 nitrate the oils less. Some operators may richen the air/fuel mixture on natural
5 gas fueled engines to increase power output and consequently increase oil
6 nitration levels. Lubricating oils with good nitration resistance are required in
7 most natural gas engine installations because the lubricating oil may be used
8 to lubricate a number of engines including stoichiometric and lean-burn
9 models.

10

11 * * *

12

13 This invention will be further illustrated by the following examples that set
14 forth particularly preferred embodiments. While the examples are provided to
15 illustrate this invention, they are not intended to limit it.

16

17 EXAMPLES

18 These examples describe experiments performed using Samples A
19 through L. Multiple experiments were performed in each example using a
20 variety of sulfonate, phenate and salicylate detergents; succinimide
21 dispersants; and zinc dithiophosphate wear inhibitors. The examples are
22 explained using the terms detergent, dispersant and wear inhibitor because
23 no significant difference was found when these components were varied.

24 Sample A was prepared by combining about 0.757 wt. % 3,5-di-t-butyl
25 4-hydroxy phenol propionate, about 3.3 wt. % dispersant, about
26 3.0 wt. % detergent, about 1.0 wt. % butylated hydroxy toluene, about
27 0.38 wt. % wear inhibitor, about 5 ppm foam inhibitor and Group I base oil
28 with agitation until all components were mixed. The ingredients were
29 combined at a temperature sufficient to blend the components but not high
30 enough to degrade the components. A temperature of about 140 degrees F.
31 was used.

32 Sample B was prepared by combining about 0.693 wt. % 3,5-di-t-butyl
33 4-hydroxy phenol propionate, about 3.3 wt. % dispersant, about

1 3.0 wt. % detergent, about 1.0 wt. % butylated hydroxy toluene, about
2 0.38 wt. % wear inhibitor, about 0.08 wt. % sulfurized isobutylene, about
3 5 ppm foam inhibitor and Group I base oil with agitation until all components
4 were mixed. The ingredients were combined at a temperature sufficient to
5 blend the components but not high enough to degrade the components. A
6 temperature of about 140 degrees F. was used.

7 Sample C was prepared by combining about 0.629 wt. % 3,5-di-t-butyl
8 4-hydroxy phenol propionate, about 3.3 wt. % dispersant, about
9 3.0 wt. % detergent, about 1.0 wt. % butylated hydroxy toluene, about
10 0.38 wt. % wear inhibitor, about 0.16 wt. % sulfurized isobutylene, about
11 5 ppm foam inhibitor and Group I base oil with agitation until all components
12 were mixed. The ingredients were combined at a temperature sufficient to
13 blend the components but not high enough to degrade the components. A
14 temperature of about 140 degrees F. was used.

15 Sample D was prepared by combining about 0.56 wt. % 3,5-di-t-butyl
16 4-hydroxy phenol propionate, about 3.3 wt. % dispersant, about
17 3.0 wt. % detergent, about 1.0 wt. % butylated hydroxy toluene, about
18 0.38 wt. % wear inhibitor, about 0.25 wt. % sulfurized isobutylene, about
19 5 ppm foam inhibitor and Group I base oil with agitation until all components
20 were mixed. The ingredients were combined at a temperature sufficient to
21 blend the components but not high enough to degrade the components. A
22 temperature of about 140 degrees F. was used.

23 Sample E was prepared by combining about 0.674 wt. % 3,5-di-t-butyl
24 4-hydroxy phenol propionate, about 3.3 wt. % dispersant, about
25 3.0 wt. % detergent, about 1.0 wt. % butylated hydroxy toluene, about
26 0.38 wt. % wear inhibitor, about 0.08 wt. % sulfurized isobutylene, about
27 5 ppm foam inhibitor and Group I base oil with agitation until all components
28 were mixed. The ingredients were combined at a temperature sufficient to
29 blend the components but not high enough to degrade the components. A
30 temperature of about 140 degrees F. was used.

31 Sample F was prepared by combining about 0.592 wt. % 3,5-di-t-butyl
32 4-hydroxy phenol propionate, about 3.3 wt. % dispersant, about
33 3.0 wt. % detergent, about 1.0 wt. % butylated hydroxy toluene, about

1 0.38 wt. % wear inhibitor, about 0.16 wt. % sulfurized isobutylene, about
2 5 ppm foam inhibitor and Group I base oil with agitation until all components
3 were mixed. The ingredients were combined at a temperature sufficient to
4 blend the components but not high enough to degrade the components. A
5 temperature of about 140 degrees F. was used.

6 Sample G was prepared by combining about 0.499 wt. % 3,5-di-t-butyl
7 4-hydroxy phenol propionate, about 3.3 wt. % dispersant, about
8 3.0 wt. % detergent, about 1.0 wt. % butylated hydroxy toluene, about
9 0.38 wt. % wear inhibitor, about 0.25 wt. % sulfurized isobutylene, about
10 5 ppm foam inhibitor and Group I base oil with agitation until all components
11 are mixed. The ingredients were combined at a temperature sufficient to blend
12 the components but not high enough to degrade the components. A
13 temperature of about 140 degrees F. was used.

14 Sample H was prepared by using OLOA 1255, commercially available
15 from Chevron Oronite Company in Houston, Texas. The OLOA 1255 was
16 mixed with Group I base oil under typical blending conditions of about
17 140 degrees F. with agitation until all components were thoroughly mixed. As
18 explained in U.S. Pat. No. 5,726,133, OLOA 1255 is one of the most widely
19 sold gas engine oil additive packages and lubricating oil comprising
20 OLOA 1255 represents a "benchmark standard" against which other
21 formulations useful as engine oils may be measured.

22 Sample I was prepared by combining about 2 wt. % sulfurized
23 isobutylene, about 6.61 wt. % dispersant, detergent, wear inhibitor and foam
24 inhibitor package and Group I base oil and agitating until all components were
25 mixed. The ingredients were combined at a temperature sufficient to blend the
26 components but not high enough to degrade the components. A temperature
27 of about 140 degrees F. was used.

28 Sample J was prepared by combining about 2 wt. % sulfurized
29 isobutylene, about 6.61 wt. % of an additive package comprising dispersant,
30 detergent, wear inhibitor and foam inhibitor with Group II base oil and
31 agitating until all components were mixed. The ingredients were combined at
32 a temperature sufficient to blend the components but not high enough to
33 degrade the components. A temperature of about 140 degrees F. was used.

1 Sample K was prepared by combining about 1.0 wt. % butylated
2 hydroxy toluene, about 6.61 wt. % of an additive package comprising
3 dispersant, detergent, wear inhibitor and foam inhibitor with Group I base oil
4 and agitating until all components were mixed. The ingredients were
5 combined at a temperature sufficient to blend the components but not high
6 enough to degrade the components. A temperature of about
7 140 degrees F. was used.

8 Sample L was prepared by combining about 1.0 wt. % butylated
9 hydroxy toluene and about 6.61 wt. % of an additive package comprising
10 dispersant, detergent, wear inhibitor and foam inhibitor with Group II base oil
11 and agitating until all components were mixed. The ingredients were
12 combined at a temperature sufficient to blend the components but not high
13 enough to degrade the components. A temperature of about
14 140 degrees F. was used.

EXAMPLE 1

The Oxidation-Nitration and Viscosity Increase Resistance Test

The Oxidation-Nitration and Viscosity Increase Resistance bench test demonstrates the capacity of lubricating oil to resist oxidation, nitration and viscosity increase. This test is a tool to help determine the performance of oils as they relate to the actual service of lubricating engines that use natural gas as a fuel source. The level of oxidation and nitration of oil, may also be compared by monitoring the viscosity increase of the oil. The lower the values for oxidation, nitration and viscosity increase at the end the test, the more superior the product's performance. The Oxidation-Nitration and Viscosity Increase Resistance bench test was designed to simulate Caterpillar 3500 series engine conditions as related to actual field performance of the Caterpillar 3516 model. Oxidation-Nitration and Viscosity Increase Resistance tests were performed on Samples A through G. The samples were placed in a heated glassware bath and subjected to calibrated levels of nitrous oxide gas over a specific period of time. The tests were run on each sample in duplicate and the results are an average of the two runs. The samples were evaluated using differential infra

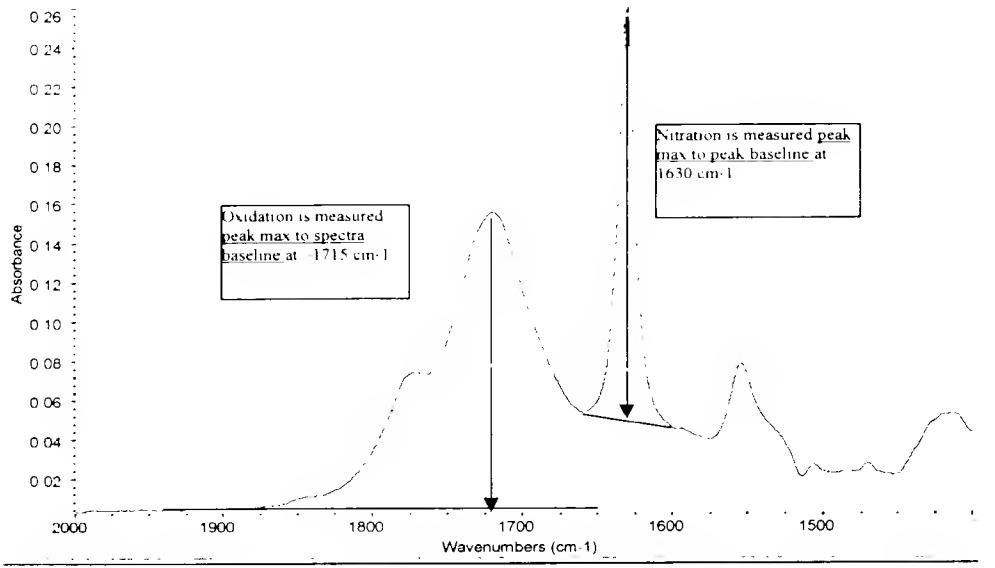
1 red spectroscopy before placing them in the heated glassware bath to
2 determine a base line for each sample. The samples were re-evaluated at the
3 end of testing period. The differential between the base line data, absorbance
4 units at 5.8 and 6.1 microns, and the data taken at the end of test cycle
5 provides an indication of the oxidation-nitration resistance of the samples.

6 Differential infra red spectroscopy measures the amount of light that is
7 absorbed by an oil sample and provides a unit of measure called an
8 absorbance unit. DIR (Differential Infrared) spectra was determined by
9 subtracting the fresh oil spectra from the used oil spectra to observe changes
10 that have occurred due to oxidation, nitration, fuel dilution, soot accumulation,
11 and or contamination. Typically a 0.1 millimeter (mm) cell is used, however an
12 ATR crystal setup may be used after determining its associated path length. If
13 the instrument does not have software that determines path length, the path
14 length may be back calculated by measuring oxidation with a calibrated
15 0.1 mm cell. The variation between ATR and vertical cell measurements is
16 minimal if restricted to the narrow area of oxidation and nitration (~1725 to
17 1630 cm⁻¹).

18 DIR Oxidation was measured from peak maximum at ~1715 ± 5 cm⁻¹ to
19 the spectra baseline (in units of absorbance).

20 DIR Nitration was measured from peak maximum at ~1630 ± 1 cm⁻¹ to
21 peak baseline (in units of absorbance).

1
2 **TABLE 3**
3 Infrared Spectra



6 Oxidation (&/or Nitration) Number Reported (abs/cm) = peak
7 absorbance divided by path length in cm^{-1} (report in whole numbers)

8 During the Oxidation-Resistance Bench Test, the viscosity increases of
9 the samples were measured at 100°C by ASTM D 445. The viscosity increase
10 is a percentage that compares the initial "fresh" kinematic viscosity with the end
11 of test "used" oil kinematic viscosity. The formula to calculate for % viscosity
12 difference is:

13
$$\% \text{ Viscosity difference} = (\text{Sample (x)}_{\text{initial}} - \text{Sample (x)}_{\text{final}}) / \text{Sample (x)}_{\text{initial}} \times 100 \%$$

16 Oxidation levels of 5.8 microns and Nitration levels of 6.1 microns were
17 used as peak height comparisons.

19 **(a) Comparison of Samples A, B, C, D, E, F, G**

20 Measurements are reported on a relative measurement basis so that
21 large results or values represent greater levels of oxidation-nitration and
22 viscosity increase resistance. Lower numbers represent shorter oil life.
23 Sample A was used as a reference oil and the results in the Tables 4 - 6 were

1 reported as a ratio in the first row of each table. This ratio was calculated by
2 dividing measurements for Sample A by the measurements taken using the
3 sample being compared to Sample A. The second row of each table displays
4 the percent difference between the reference Sample A and the samples being
5 compared to Sample A. The larger the percentage difference between
6 Sample A and the other samples, the better performing the sample in respect to
7 parameter being compared. Sample A was the reference sample for the results
8 reported in Table 4-6. The formula to calculate percentage difference of the
9 ratios compared to Sample A for Tables 4-6 is:

10

11 % difference = (Sample (x) – Sample A)/Sample (x) x 100 %

12

13

Table 4

14

Oxidation Resistance Test Results

	Sample A	Sample B	Sample C	Sample D	Sample E	Sample F	Sample G
Ratio*	1.00	1.32	1.39	1.25	1.78	1.02	1.22
% Difference compared to Sample A**	0	24	28	20	44	2	18

15

*Ratio – These numbers are relative ratios compared to Sample A's performance in this test. Numbers larger than 1.00 perform better than Sample A and less than 1.00 perform worse than the reference. The higher the ratio number, the higher the performance of the sample.

16

**% Difference – These numbers are the percentage differences between Sample A and the comparative Sample. A negative number indicates worse performance than Sample A.

17

18

19

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22

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26

27

The results presented in Table 4 indicate that Samples B through G exhibited at least a 2 % to 44 % improvement in oxidation resistance over the reference Sample A. Sample E performed better in oxidation resistance than any other sample tested.

1
2 **TABLE 5**
3 **Nitration Resistance Test Results**

	Sample A	Sample B	Sample C	Sample D	Sample E	Sample F	Sample G
Ratio*	1.00	1.60	1.02	1.33	1.88	1.43	1.32
% Difference compared to Sample A**	0	38	2	25	47	30	24

3 *Ratio – These numbers are relative ratios compared to Sample A's performance in this test. Numbers larger than
4 1.00 perform better than Sample A and less than 1.00 perform worse than the reference. The higher the ratio
5 number, the higher the performance of the sample.

6 **% Difference – These numbers are the percentage differences between Sample A and the comparative Sample A
7 A negative number indicates worse performance than Sample A

10 The results in Table 5 indicate improved performance of
11 Samples B through H over the reference sample A. The improvement ranged
12 from 2 % to 47 % over the reference Sample A in nitration resistance. Again,
13 Sample E performed better with respect to nitration resistance than all the
14 other samples tested.

15
16 **TABLE 6**
17 **Viscosity Increase Resistance Test Results**

	Sample A	Sample B	Sample C	Sample D	Sample E	Sample F	Sample G
Ratio*	1.00	1.19	1.58	1.38	1.70	1.02	1.24
% Difference compared to Sample A**	0	16	37	28	41	2	19

18 *Ratio – These numbers are relative ratios compared to Sample A's performance in this test. Numbers larger than
19 1.00 perform better than Sample A and less than 1.00 perform worse than the reference. The higher the ratio
20 number, the higher the performance of the sample.

21 **% Difference – These numbers are the percentage differences between Sample A and the comparative Sample A
22 A negative number indicates worse performance than Sample A

26 The results in Table 6 indicate that Samples B through G performed
27 better than reference Sample A. The improvement ranged from 2 % to
28 41 % over the reference sample in viscosity increase resistance.

29 Sample E performance was better than the reference sample with
30 respect to oxidation, nitration and viscosity increase. Sample E performed
31 better than all the samples tested with respect to minimizing the levels of
32 oxidation, nitration and viscosity increase. These tests quantify a lubricating
33 oil's resistance to oxidation, nitration and the resultant viscosity increase and

1 are used to determine whether samples are good candidates for extending
2 the life of lubricating oil particularly those lubricating oils for use in natural gas
3 fueled engines. Absorbing oxygen and nitrogen and the resultant viscosity
4 increase associated with absorbing oxygen and nitrogen are undesirable for
5 lubricating oil particularly lubricating oils for use in natural gas fueled engines.

6

7 **(b) Comparison of Samples I and K**

8 The Oxidation-Nitration and Viscosity Increase Resistance bench test
9 demonstrates the capacity of lubricating oil to resist oxidation, nitration and
10 viscosity increase. The Oxidation-Nitration and Viscosity Increase Resistance
11 tests described in Example 1 were performed on Samples I and K.

12 Measurements are reported on a relative measurement basis so that
13 large results or values represent greater levels of oxidation-nitration and
14 viscosity increase resistance. Lower numbers represent shorter oil life.
15 Sample K was used as a reference oil and the results in the Tables 7 – 9 were
16 reported as a ratio in the first row of each table. This ratio was calculated by
17 dividing measurements for Sample K by the measurements taken using the
18 sample being compared to Sample K. The second row of each table displays
19 the percent difference between the reference Sample K and Sample I being
20 compared to Sample I. The larger the percentage difference between
21 Sample K and Sample I, the better performing the sample in respect to
22 parameter being compared. Sample K was the reference sample for the results
23 reported in Table 7 – 9. The formula to calculate percentage difference of the
24 ratios compared to Sample K for Tables 7 - 9 is:

25

26 % difference = (Sample (x) – Sample K)/Sample (x) × 100 %

27

1

2

TABLE 7

Oxidation Resistance Test Results

	Sample K	Sample I
Ratio*	1.00	1.76
% Difference compared to Sample K**	0	43

3

4 *Ratio – These numbers are relative ratios compared to Sample K's performance in this test. Numbers larger than
5 1.00 perform better than Sample K and less than 1.00 perform worse than the reference. The higher the ratio
6 number, the higher the performance of the sample.

7

8 **% Difference – These numbers are the percentage differences between Sample K and the comparative Sample. A
9 negative number indicates worse performance than Sample K.

10

11 The results presented in Table 7 indicate that Sample I exhibited a
12 43 % improvement in oxidation resistance over the reference Sample K.

13

14

15

TABLE 8

Nitration Resistance Test Results

	Sample K	Sample I
Ratio*	1.00	1.96
% Difference compared to Sample K**	0	49

16 *Ratio – These numbers are relative ratios compared to Sample K's performance in this test. Numbers larger than
17 1.00 perform better than Sample K and less than 1.00 perform worse than the reference. The higher the ratio
18 number, the higher the performance of the sample.

19

20 **% Difference – These numbers are the percentage differences between Sample K and the comparative Sample. A
21 negative number indicates worse performance than Sample K.

22

23 The results presented in Table 8 indicate that Sample I exhibited a
24 43 % improvement in nitration resistance over the reference Sample K.

25

1
2 **TABLE 9**
Viscosity Increase Resistance Test Results

	Sample K	Sample I
Ratio*	1.00	1.73
% Difference compared to Sample K**	0	42

3 *Ratio – These numbers are relative ratios compared to Sample K's performance in this test. Numbers larger than
4 1.00 perform better than Sample K and less than 1.00 perform worse than the reference. The higher the ratio
5 number, the higher the performance of the sample.

6
7 **% Difference – These numbers are the percentage differences between Sample K and the comparative Sample. A
8 negative number indicates worse performance than Sample K

9
10 The results presented in Table 9 indicate that Sample I exhibited a
11 42 % improvement in viscosity increase resistance over the reference
12 Sample K.

13 Sample I performance was better than the reference sample with
14 respect to oxidation, nitration and viscosity increase. Sample I performed
15 better than Sample K tested with respect to minimizing the levels of oxidation,
16 nitration and viscosity increase.

17
18 (c) Comparison of Samples J and L

19 The Oxidation-Nitration and Viscosity Increase Resistance bench test
20 demonstrates the capacity of lubricating oil to resist oxidation, nitration and
21 viscosity increase. This test is the same as described in
22 Example 1. Oxidation-Nitration and Viscosity Increase Resistance tests were
23 performed on Samples J and L. The test was run and analyzed as described in
24 Example 1. Samples J and L were tested in the test described in
25 Example 1. The oxidation and nitration of the samples were analyzed using
26 differential IR as described in Example 1. Viscosity Increase of the samples
27 was monitored by using the Viscosity Increase test described in Example 1.

28 Measurements are reported on a relative measurement basis so that
29 large results or values represent greater levels of oxidation-nitration and
30 viscosity increase resistance. Lower numbers represent shorter oil life.

31 Sample L was used as a reference oil and the results in the Tables 10 – 12
32 were reported as a ratio in the first row of each table. This ratio was calculated
33 by dividing measurements for Sample L by the measurements taken using the

1 sample being compared to Sample L. The second row of each table displays
2 the percent difference between the reference Sample L and Sample J being
3 compared to Sample J. The larger the percentage difference between
4 Sample L and Sample J, the better performing the sample in respect to
5 parameter being compared. Sample L was the reference sample for the results
6 reported in Table 10 – 12. The formula to calculate percentage difference of the
7 ratios compared to Sample L for Tables 10 - 12 is:

8

9 % difference = (Sample (x) – Sample L)/Sample (x) x 100 %

10

11

TABLE 10
Oxidation Resistance Test Results

	Sample L	Sample J
Ratio*	1.00	1.55
% Difference compared to Sample L**	0	36

13 *Ratio – These numbers are relative ratios compared to Sample L's performance in this test. Numbers larger than
14 1.00 perform better than Sample L and less than 1.00 perform worse than the reference. The higher the ratio number,
15 the higher the performance of the sample.

16 **% Difference – These numbers are the percentage differences between Sample L and the comparative Sample. A
17 negative number indicates worse performance than Sample L.

18

20 The results presented in Table 10 indicate that Sample J exhibited a
21 36 % improvement in oxidation resistance over the reference Sample L.

22

23

TABLE 11
Nitration Resistance Test Results

	Sample L	Sample J
Ratio*	1.00	5.42
% Difference compared to Sample L**	0	82

25 *Ratio – These numbers are relative ratios compared to Sample L's performance in this test. Numbers larger than
26 1.00 perform better than Sample L and less than 1.00 perform worse than the reference. The higher the ratio number,
27 the higher the performance of the sample.

28 **% Difference – These numbers are the percentage differences between Sample L and the comparative Sample. A
29 negative number indicates worse performance than Sample L.

30

32 The results presented in Table 11 indicate that Sample J exhibited a
33 82 % improvement in nitration resistance over the reference Sample L.

1

2 TABLE 12

3

Viscosity Increase Resistance Test Results

	Sample L	Sample J
Ratio*	1.00	3.38
% Difference compared to Sample L**	0	70

4 *Ratio – These numbers are relative ratios compared to Sample L's performance in this test. Numbers larger than
 5 1.00 perform better than Sample L and less than 1.00 perform worse than the reference. The higher the ratio number,
 6 the higher the performance of the sample

7 **% Difference – These numbers are the percentage differences between Sample L and the comparative Sample. A
 8 negative number indicates worse performance than Sample L.

10

11 The results presented in Table 12 indicate that Sample J exhibited a
 12 70 % improvement in viscosity increase resistance over the reference
 13 Sample L.

14 Sample J performance was better than the reference Sample L with
 15 respect to oxidation, nitration and viscosity increase.

16 These tests quantify a lubricating oil's resistance to oxidation, nitration
 17 and the resultant viscosity increase and are used to determine whether
 18 samples are good candidates for extending the life of lubricating oil
 19 particularly those lubricating oils for use in natural gas fueled engines.

20 Absorbing oxygen and nitrogen and the resultant viscosity increase
 21 associated with absorbing oxygen and nitrogen are undesirable for lubricating
 22 oil particularly lubricating oils for use in natural gas fueled engines.

23

24

EXAMPLE 2

25

Comparing Samples E and H

26 Because the Caterpillar 3500 series natural gas fueled engines are one
 27 of the most commonly used and one of the most severe engines with respect
 28 to oil life, they were used as a tool to determine the life of lubricating oil.

29 These tests were run in the same Caterpillar 3512 engine to minimize the
 30 amount of variables that are introduced in the testing environment. Oil life as
 31 used herein is the length of time it takes for a lubricating oil to reach
 32 Caterpillar's condemning limits for natural gas fueled engine lubricating oil. At
 33 the time of testing the Caterpillar limits are presented in Table 13.

1

2 **TABLE 13**

3 Caterpillar Limits at Time of Testing

Test	Caterpillar Limit
Oxidation	25 abs/cm ⁻¹ by differential infra red spectroscopy
Nitration	25 abs/cm ⁻¹ by differential infra red spectroscopy
Viscosity Increase	3 cSt increase over fresh oil
Total Base Number (TBN)	50 % of fresh oil TBN by ASTM D2896
Total Acid Number (TAN)	2.0 number increase over the fresh oil or 3.0 maximum TAN by ASTM D664

4

5 Both samples were run in the Caterpillar 3512 until the condemning

6 limits were exceeded. The oxidation and nitration of the samples were

7 analyzed using differential IR as described in Example 1. Viscosity Increase of

8 the samples was monitored. The Viscosity Increase analysis is described in

9 Example 1. Sample E exhibited better performance with respect to oxidation,

10 nitration and viscosity increase than Sample H. Total Base Number (TBN) and

11 Total Acid Number (TAN) analyses were also performed. TBN refers to the

12 amount of base equivalent to milligrams of KOH in one gram of sample. Thus,

13 higher TBN numbers reflect more alkaline products, and therefore a greater

14 alkalinity reserve. The TBN of a sample may be determined by

15 ASTM Test No. D2896. TAN refers to the amount of acid equivalent to

16 milligrams of Potassium Hydroxide (KOH) in 1 gram of sample. TAN was

17 determined by the procedure described in ASTM D664.

18 Samples E and H were tested separately by using each one as a

19 lubricant in the same Caterpillar 3512 natural gas fueled engine for a total

20 time of over 5 months. The oxidation and nitration of the samples were

21 analyzed using differential IR as described in Example 1. Viscosity Increase of

22 each sample was monitored by using the Viscosity Increase test described in

23 Example 1. Total Base Number (TBN) and Total Acid Number (TAN) analyses

24 were also performed as described above.

25 Sample E oil life performance was better than that of Sample H. Both

26 samples were formulated in Group I base oil. TBN and TAN performance are

27 parameters that are typically used to decide when to condemn lubricating oil.

28 Sample E had an increased oil life of 75 % and 79 %, respectively, when

29 compared to Sample H.

1 The calculation formula for Relative Percent Improvement for
2 Table 14 is:

3
4 Relative Percent Improvement =
5 (Sample E – Sample H)/Sample H x 100 % of sulfurized isobutylene in a finished oil formulation.
6

7 TABLE 14

	Sample E	Sample H
Hours to Reach Caterpillar Limit for Oxidation	1100	900
Relative Percent Improvement Comparison to Sample H for Oxidation	22.2	0
Hours to Reach Caterpillar Limit for Nitration	1250	855
Relative Percent Improvement Comparison to Sample H for Nitration	46.7	0
Hours to Reach Caterpillar Limit for Viscosity Increase	1085	900
Relative Percent Improvement Comparison to Sample H for Viscosity Increase	20.6	0
Hours to Reach Caterpillar Limit for TBN	1175	670
Relative Percent Change Improvement Comparison to Sample H for TBN	75.4	0
Hours to Reach Caterpillar Limit for TAN	1300	725
Relative Percent Improvement Comparison to Sample H for TAN	79.3	0

8
9 These results demonstrate that the lubricating oil compositions
10 comprising the antioxidant system of this invention show high resistance to
11 oxidation, nitration and viscosity increase.

12 While the invention has been described in terms of various
13 embodiments, the skilled artisan will appreciate that various modifications,
14 substitutions, omissions and changes may be made without departing from
15 the spirit thereof.